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SOURCES OF ERROR IN THE DETERMINATION OF THE ATOMIC WEIGHT OF NITROGEN.

(Contribution from the Chemical Laboratory of Harvard College.)

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(*Read April 7, 1904.*)

The combining weight of nitrogen presents a problem of unusual interest, because of the uncertainty which still clings to it, in spite of the careful work of some of the most accurate of chemical experimenters. Uncertainty of this kind implies a lack of comprehension of some unknown variable or variables, and it is always possible that the determination of these variables may lead to the discovery of some new important fact or principle. Thus the accurate work of Lord Rayleigh in demonstrating that the less active gases of the atmosphere are somewhat heavier than pure nitrogen, led to the discovery of argon and the other inert gases.

The data for computing the atomic weight of nitrogen are manifold, because nitrogen enters into many well-defined compounds. Unfortunately, however, it is always necessary to find the weight of the nitrogen indirectly. The most extended series of experiments was instituted by the great Belgian chemist Stas, who attacked the problem in various ways, converting silver into the nitrate, converting this nitrate into chloride, converting the nitrates of potassium and sodium into chlorides, and comparing ammonic chloride and bromide with pure silver. The average results of these experiments have been variously computed, the extreme estimates of the atomic weight of nitrogen ranging between 14 039 and 14.058 if the atomic oxygen is taken as 16.000.[1]

[1] The early work of Stas involving argentic chloride must all be rejected, because insufficient precautions were taken concerning its solubility. Among the other pertinent data obtained by him the following, easily traced in Clarke's convenient *Recalculation of the Atomic Weights* (1897), seem to me the most important.

(O = 16.000; A_g = 107.930; Cl = 35.455, H = 1.0076, Br = 79.955)

100.000 parts of silver gave 157.478 of its nitrate.....N = 14.036
100.000 parts of silver correspond to 49.599 of ammonic chloride..N = 14.047
100.000 parts of silver correspond to 90.830 of ammonic bromide..N = 14.048
Difference between molecular weights of alkaline nitrates and chlorides = 26.589.....N = 14.043

Marignac's work on argentic chloride and nitrate leads to a much lower value

Stas himself concluded from these results that nitrogen was almost certainly higher than 14.03, and probably about 14.045, basing his conclusion upon a somewhat doubtful application of the theory of least squares.[1]

In spite of the great care taken by Stas in this unusually extended investigation, it is of course not impossible that small constant errors might have existed in parts of the work. Stas was by no means infallible; his long oversight of the solubility of argentic chloride, the uncertainty concerning the amount of oxygen occluded by his silver, and his frequent use of glass vessels somewhat attacked by his reagents for long-continued operations, being among the evidences that he too was mortal. Nevertheless, it is true that Stas was more precise than any one who preceded him; and his results cannot be overthrown without much conclusive experimental evidence.

Three years ago the accuracy of one of these series[2] of experiments made by Stas was impugned by Alexander Scott, namely, the series in which ammonic bromide was compared with silver. The atomic weight is computed from the result of these experiments by subtracting the weight of the bromine precipitated as silver bromide from the weight of the ammonium bromide, in order to find the weight of ammonium present. Because the bromine is equivalent to the silver, the ammonium previously united to the bromine must also be equivalent, and upon assuming the atomic weight of silver to be 107.93, the molecular weight of ammonium is easily found to be 18.078. Subtracting from this four times the atomic weight of hydrogen, that of nitrogen remains—namely, 14.048 — because ammonium consists solely of nitrogen and hydrogen.

Now Scott contended, with plausibility, that this particular specimen of ammonium contained impurities, substances other than nitrogen and hydrogen, because Stas admits that his bromide was not perfectly colorless.

These impurities would all be included in the estimate of the

for nitrogen (14.01 to 14.02), a discrepancy which it is not easy to explain, unless the chloride was precipitated from a solution so concentrated as to occlude nitrate. The lack of details in his description makes it impossible to decide this question.

[1] Stas, *Untersuchungen* (Aronstein), p. 322 (1867).

[2] *J. Chem. Soc. Trans.*, *79*, 147 (1901).

weight of the nitrogen, since this is merely the remainder left after subtracting that of the bromine and the hydrogen. Hence, Stas's estimate of the atomic weight of nitrogen is probably too high—how much too high it is impossible at once to decide. Some of the possible impurities have so powerful a color that an inappreciable weight of them might darken visibly an otherwise pure sample of salt; but an inappreciable weight could not affect the combining proportion, hence the error may be negligible.

In any case it is obviously well that Stas's experiments on ammonic bromide should be verified; and the repetition was undertaken by Scott. His ammonium preparation was purified, as he states, by drastic methods, and was beautifully clear and colorless. There is little doubt that, so far as the ammonium was concerned, the salt was purer than Stas's. Unfortunately, however, in his anxiety to purify the ammonium, Scott evidently neglected to purify adequately the bromine which he combined with it. His own results prove this fact indubitably, for he found on the average[1] that 107.93 parts of silver combined with only 79.943 parts of his bromine,[2] a figure perceptibly lower than the most probable value, 79.955. This latter value, computed from Stas's work, has been repeatedly verified in the Chemical Laboratory of Harvard College during the last twelve years with only very slight variations. In order to show how definite the figure is, there is given below a table of all our most refined recent work on this ratio.[3]

[1] Neglecting one imperfect experiment, *J. Chem. Soc. Trans.*, *79*, 147 (1901).

[2] Even this weight of bromine may have been too high, since Scott apparently overlooked the danger of the inclusion of water by the argentic bromide (*Proc. Am. Phil. Soc.*, 1903, 28). The fused substance is the only safe standard of reference. In this connection it should be noted that an impurity in Scott's silver would have caused an error in the same direction. Scott seems to have taken more pains with his silver than with his bromine, although indeed he condemns on the basis of a single analysis a method of fusing it which many others have found satisfactory (*J. Chem. Soc. Trans.*, *79*, 15, 1901).

[3] Clarke's similar table, *Recalc.*, p. 46 (1897), is necessarily incomplete and includes some imperfect preliminary results, besides containing several minor mistakes in calculation.

Compound containing Bromine analyzed.	No. of experiments.	Analyst.	Reference Proc. Am. Acad.	Per cent. of silver in AgBr.
$BaBr_2$	Last seven	Richards	*28*, 28, 29	57.444
$SrBr_2$	Seven	"	*30*, 389	57.444
$ZnBr_2$	Last series	"	*31*, 178	57.445
$NiBr_2$	Last seven	Cushman	*33*, 111	57.444
$CoBr_2$	Last five	Baxter	*33*, 127	57.446
UBr_4	Three	Merigold	*37*, 393	57.447
HBr	Two	Richards	*28*, 17	57.445
"	One	"	*30*, 380	57.446
"	Two	"	*31*, 165	57.444
"	One	Cushman	*33*, 106	57.445
"	One	Baxter	*33*, 122	57.444
"	Two	Baxter	*34*, 353	57.447
Average				57.4451

This percentage of silver in argentic bromide corresponds to an atomic weight of 79.954 for bromine, if silver is taken as 107.93; and in my opinion this value is if anything rather too low than too high, because most of the probable errors tend to diminish it.

This value agrees almost exactly with that of Stas's work, and hence there seems little room for doubt that if silver is 107.93 bromine is between 79.95 and 79.96. Therefore Scott's bromine (79.943) must have been impure, probably containing chlorine, which is not easy to eliminate. It is also possible that the argentic bromide was precipitated from too concentrated a solution and hence contained nitrate. This error would have affected the result in the same way.

If there were no error in determining the amount of silver needed for the precipitation, it would be easy nevertheless to correct for this impurity of the bromine in the following way. Scott found that 107.93 parts of silver corresponded to 97.995 parts of ammonic halide and 79.943 parts of halogen. By subtracting the last figure from the one preceding it the molecular weight of ammonium is found, independent of the nature of the halogen, to be 18.052, and hence that of nitrogen 14.022. This value is considerably higher than that calculated by Scott on the assumption that his ammonic bromide was perfectly pure. Unfortunately, however, the presence of chlorine in the salt, by introducing the partly soluble argentic chloride, complicates both the determination of the amount of silver required for the precipitation and the collection of the salt of

silver for weighing. Scott seems to have taken no especial precautions as regards either of these complications, hence the possible error of his work, even when corrected in the manner described above, is as great as the difference between his work and that of Stas. Thus it cannot be said to militate against that work, except in pointing out that it is possible to obtain colorless ammonic bromide.

Scott also performed two analyses of ammonic chloride, which gave a result (14.031) more nearly like that of Stas than that from the bromide, but likewise somewhat lower. Since the analyses are hardly numerous enough to be conclusive, and since no especial pains seems to have been taken to prevent the injurious effect of the solubility of argentic chloride or the inclusion of argentic nitrate in the precipitate, no further attention need be given to this result, although it must be considered as more satisfactory than the preceding work on the bromide.

No light is shed upon the doubtful situation by the conclusions of D. Berthelot[1] and of Leduc[2] concerning the density of nitrogen, since they depend upon the precise fulfillment of the rule of Avogadro, a generalization which is undoubtedly only an approximation.[3]

Other recently published results are recorded in the table below.

Thomsen (*Zeitschr. Phys. Chem.*, *13*, 398, 1894)	14.021
Hardin (*J. Am. Ch. Soc.*, *18*, 990, 1896)	14.01
Hibbs (Thesis, U. of Pa., 1896)	14.01
Dean (*J. Chem. Soc. Trans.*, *77*, 117, 1900)	14.031
Ramsay and Aston (*Gesell. d. Naturforscher und Aerzte, Allg. Th.* (1903) 8)	13.903
Richards and Archibald (*Proc. Am. Acad.*, *38*, 469, 1903)	14.039

Thomsen's result was obtained by weighing the hydrochloric acid and ammonia required to neutralize one another. In my recent experiments on the atomic weight of magnesium, in coöperation with Prof. H. G. Parker, it was found that hydrochloric acid gas is by no means easy to dry thoroughly. It is therefore not impossible that Thomsen weighed some water with his acid, thus causing the weight of ammonia, and hence of nitrogen, to appear too low.

[1] *Comp. Rend.*, *126*, 954, 1030, 1415 and 1501 (1898).

[2] Leduc, *Comp. Rend.*, *125*, 299 (1897).

[3] Ramsay and Steele, *Phil. Mag.*, Oct., 1903, p. 492.

Among the other investigations those of Hardin and Hibbs were very carefully carried out, but the quantities of material used were so small that these experiments could hardly be expected to determine accurately the second decimal place of the atomic weight. They each weighed portions of substance containing on the average only about 0.05 gram of nitrogen, and hence to be certain of a unit in the second decimal place of the atomic weights the weighing must be certain to within 0.00003 gram. Such precision is almost impossible when one is using a vessel weighing 71 grams, as Hardin did. Moreover, Hardin seems to have made no correction for the trace of electrolyte included in the film of silver which formed one of his standards of reference.

The work of Dean depended upon the volumetric analysis of argentic cyanide. The method of work was too indirect to carry great weight, even if volumetric analysis were at best a process accurate enough for the degree of precision needed.

The work of Sir William Ramsay and Miss Aston is interesting because it involved the analysis of unstable compounds of azoimide. The extraordinarily low result, a whole per cent. less than the usually accepted value, is not easily explained. The authors tentatively suggest once more the revolutionary assumption that the chemical combining proportions are not constant. This idea is by no means a new one, having been seriously advanced by J. P. Cooke in 1855[1] and again by Butlerov in 1882.[2] In both these older cases it is now fairly certain that there is no need of such an iconoclastic assumption; in Cooke's zinc antimonide crystals the solid solution of excess of antimony or zinc in the crystals was probably the cause of the observed irregularities, and in Butlerov's case the analytical data upon which the conclusions rested were probably faulty. Much more recently the experiments of Heydweiler have suggested that possibly a slight change in weight may take place during chemical reaction; but the changes which he observed are so small as to be of entirely another order from this deficiency of a whole per cent. in nitrogen. On studying Ramsay and Aston's work it seems not impossible that the hydrolysis and slightly reducing action of the weak and unstable nitrohydric acid,[3] may have caused a deficiency of nitrogen in the salts which they

[1] *Mem. Am. Acad.*, V, 23 (1855).

[2] *Chem. Centralblatt, 1882*, 740.

[3] Curtius and Radenhausen, *J. Pr. Chem.* (2), *43*, 207 (1891).

analyzed, and thus may have led to an underestimate of its atomic weight. Nevertheless, the case is one of those exceptional ones which needs further investigation before it can be cast wholly aside.

At that time, by request of Sir William Ramsay, I made some preliminary experiments upon entirely a new method, namely, the conversion of sodic carbonate into nitrate. These led to a value at least 14.02 for the quantity in question, thus concurring rather with the usually accepted value than with the widely deviant results of the English experimenters. This work has not been completed, and therefore need not receive further discussion.

Still more recently, in connection with Dr. E. H. Archibald, still another method was tried with success.[1] The nitrates of potassium and cæsium were decomposed by finely divided pure silica, the nitric acid being completely expelled. If the atomic weights of these two metals are assumed to be respectively 39.139 and 132.879 (values calculated from other accurate data), that of nitrogen is found to be in the two cases respectively 14.037 and 14.040, in good confirmation of the work of Stas upon the nitrates. Viewed as a means of determining the atomic weight of nitrogen, these analyses must nevertheless be regarded as preliminary, since hardly large enough quantities of material were taken to attain the best results, although indeed the average amount of nitrogen weighed was ten times as great as that weighed by some of the previously mentioned experimenters. The real purpose in this case was to determine the atomic weight of cæsium by a wholly new method, assuming nitrogen to be known.

On considering all these data and their possible errors discussed above it seems probable that the atomic weight of nitrogen is not less than 14.02 and not over 14.04, probably being nearer to the latter value than to the former. The occasional wide deviations are not certain enough to demand the assumption of inconstancy in the atomic weights, or the necessity of disbelieving in the law of the conservation of weight; but the irregularities which exist are enough to point to the desirability of further investigation. Such investigation could hardly fail to yield an interesting outcome, since any uncomprehended relation in nature must be due to some fact or facts not hitherto recognized.

[1] Richards and Archibald, *Proc. Am. Acad.*, *38*, 458 (1903).